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(NASA-CR-125429) CARBON OXIDATION KINETIC
STUDIES USING METHODS OF FREQUENCY RESPONSE
W.J. Stenger, et al (Pittsburgh Univ.)
1969

N72-70305

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NGL-39-011-002
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CARBON OXIDATION KINETIC STUDIES
USING METHODS OF FREQUENCY RESPONSE

by

William J. Stenger and Alan J. Brainard
Department of Chemical and Petroleum Engineering
University of Pittsburgh
Pittsburgh, Pennsylvania 15213

ABSTRACT

A finite difference program has been developed which permits computer simulation of complex flow reaction systems in packed bed reactors. Reactions of the form $A(g) + E(s) \rightarrow P_i(g)$ may be investigated along with side reactions, adsorption and desorption of reactants and products. Reactant and product concentrations as functions of time and position are calculated from given inlet conditions.

Specifically, the oxidation of carbon by an oxygen stream is studied.

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
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	CR-125429	
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I. INTRODUCTION

A. Background of the Problem

Because of its importance as a world energy source the gas-solid reaction, specifically that of the oxidation of solid carbon, has long been the subject of much investigation and discussion. More recently, advances in catalysis and the advent of the catalytic reactor for the control of automotive exhaust emissions have spurred interest in the study of the gas-solid reactions in packed bed reactors, and increased the need for more rigorous design of catalytic reactors.

The study of gas-solid reactions in a packed bed is complicated by the number of phenomena which take place. Aside from the flow of gases through the bed as well as the possibility of reactions in the gas phase, there is simultaneous mass transfer of each species between the fluid and the solid along with possible reactions of the adsorbed species on the solid particles. As a result, even the simplest systems are often too complex to yield analytical solutions.

For example, consider the case of a single gaseous reactant A which reacts with a solid B in a packed bed reactor to form n gaseous products P_i :



The flow of each gaseous species is described by a second order partial differential equation which will, in general,

be nonlinear if there are any reactions in the gas stream involving the products and/or reactant. Furthermore, for each gaseous species a first order partial differential equation is needed to describe the adsorption, desorption and reactions on the solid surface. The resulting set of $2(n+1)$ simultaneous partial differential equations will be coupled through the reaction terms and generally will be too complex to solve analytically.

B. Statement of the Problem

The primary purpose of this paper is to develop a general method of solving for the individual species concentrations in a packed bed reactor. A finite difference approach is developed for this purpose. This method permits adsorption, desorption and/or reaction of each species on the solid surface as well as product-reactant and product-product reactions in the fluid phase. The secondary objective is to study the carbon oxidation reaction prior to the initiation of an experimental program. Accordingly, the parameters which have the greatest influence on the system can be isolated before any experimental work is done.

In both instances, it is desired that for any given set of input parameters the concentration of each species in the fluid phase can be obtained as a function of time for various positions in the packed bed. Furthermore, an analysis of the moments of the system is desired because of their usefulness for modeling important system properties.

The mathematical model used in this work is basically the Dispersion Model with additional terms added to account for mass transfer at the solid surface and gas phase reactions. Bischoff and Levenspiel (1) have presented a complete review of this model.

II. MATHEMATICAL TREATMENT

A. Generalized Fluid Dispersion Model

The system under consideration is a packed bed chemical reactor through which a mixture of gases of known composition is flowing. The surface concentration of each gas adsorbed on the solid particles is in dynamic equilibrium with the gas in the fluid phase. At the inlet of the reactor, a pulse of known composition is introduced. The gases in the pulse may be adsorbed, desorbed and/or reacted at the solid surface. It is also possible that reactions may take place in the fluid phase.

For a pulse consisting of n gaseous species, assuming constant dispersion coefficients and no variation in the radial direction, a material balance for each species taken over a differential segment of the reactor yields:

$$D_i \frac{\partial^2 C_i}{\partial x^2} - v_i \frac{\partial C_i}{\partial x} - \frac{\partial C_i}{\partial \theta} + S_i + r_i = 0 \quad i = 1, \dots, n \quad (1)$$

The source/sink term from equation (1) may be expressed as:

$$S_i = -\frac{1}{\alpha} \frac{\partial w_i}{\partial \theta} \quad (2)$$

To solve equations (1) and (2) it is necessary to relate the rate of adsorption, equation (2) to the gas stream concentration, C_i .

It has been shown by Chao and Hoelscher (2) that the rate of adsorption on the solid surface could be related to the gas stream concentration by:

$$-S_i = \frac{1}{\alpha} \frac{\partial w_i}{\partial \theta} = \frac{1}{R_i} (C_i - C_i^*) \quad i = 1, \dots, n \quad (3)$$

In order to relate the equilibrium concentration, C_i^* , to the adsorbate concentration at the surface, w_i , Chao and Hoelscher assumed that for low concentrations a linear isotherm could be used. In addition, if a reaction occurs at the solid surface, equation (3) will have the form:

$$-S_i = \frac{1}{\alpha} \frac{\partial w_i}{\partial \theta} = \frac{1}{R_i} \left(C_i - \frac{w_i}{B_i} \right) + r_{si} \quad i = 1, 2, \dots, n \quad (4)$$

The problem is now one of solving equations (1) and (4) for the adsorbed and fluid phase concentrations. To do this it is necessary to express fluid phase and adsorbed phase reaction rates in terms of fluid and adsorbed species concentrations. Hence it is necessary to formulate a reaction model.

B. The Carbon Oxidation Model

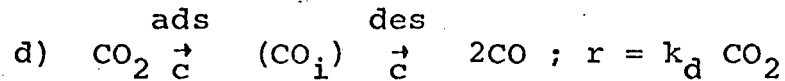
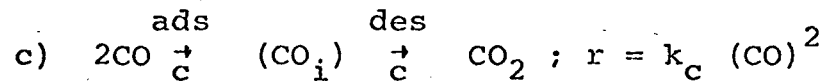
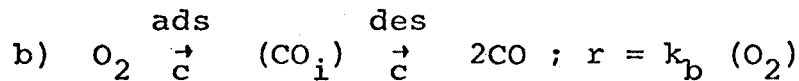
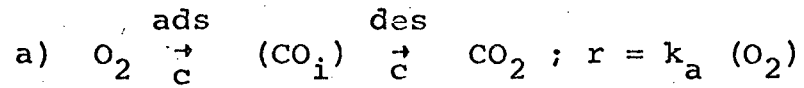
Consider a packed bed chemical reactor whose packing consists of solid carbon particles. The fluid pulse flowing through the reactor is made up of oxygen, carbon monoxide and/or carbon dioxide. The following assumptions are made:

1) O_2 , CO , and CO_2 are all adsorbed on the surface of the carbon particles.

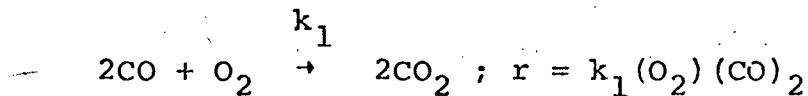
2) O_2 , CO , and CO_2 may all be desorbed without undergoing reaction.

3) Possible reactions on the solid surface are

(3), (4);



4) The only possible reaction in the fluid stream is:



5) The rates of reaction on the solid particles are dependent upon adsorption and desorption.

6) The void fraction, α , is unchanged by the reaction.

The reaction rates may now be expressed in terms of concentration and rate constant using assumptions (1) to (6). However, before any solution is attempted the variables in equations (1) and (4) will be expressed in dimensionless form.

C. Dimensionless Form

The set of equations (1) and (4) will be expressed in dimensionless form by means of suitable substitutions to

facilitate their solution. For convenience define:

$$a = (O_2), b = (CO), c = (CO_2), d = (\hat{O}_2), e = (\hat{CO}),$$

$$f = (\hat{CO}_2) \text{ where } \hat{\ } \text{ indicates the adsorbed species.}$$

Next the following dimensionless variables are introduced:

$$\begin{aligned} Y &= \frac{x}{L} & B &= b/b_o \\ Pe_i &= \frac{VL}{D_i} & C &= c/c_o \\ t &= \frac{V\theta}{L} & D &= d/d_o \\ A &= a/a_o & E &= e/e_o \\ & & F &= f/f_o \end{aligned}$$

where subscript, o, refers to a reference concentration. Upon substitution into equations (1) and (4), the following set of dimensionless partial differential equations result:

$$\begin{aligned} \frac{1}{Pe_A} \frac{\partial^2 A}{\partial y^2} - \frac{\partial A}{\partial y} - \frac{\partial A}{\partial t} - \frac{d_o}{\alpha a_o} \frac{\partial D}{\partial t} - \frac{k_1 b_o^2 L}{V} AB^2 &= 0 \\ \frac{1}{Pe_B} \frac{\partial^2 B}{\partial y^2} - \frac{\partial B}{\partial y} - \frac{\partial B}{\partial t} - \frac{e_o}{\alpha b_o} \frac{\partial E}{\partial t} - \frac{2k_1 a_o b_o L}{V} AB^2 &= 0 \\ \frac{1}{Pe_C} \frac{\partial^2 C}{\partial y^2} - \frac{\partial C}{\partial y} - \frac{\partial C}{\partial t} - \frac{f_o}{\alpha e_o} \frac{\partial F}{\partial t} + \frac{2k_1 a_o b_o^2 L}{C_o V} AB^2 &= 0 \end{aligned} \quad (5)$$

and;

$$\begin{aligned} \frac{V}{\alpha L} \frac{\partial D}{\partial t} &= \frac{1}{R_A} \left(\frac{a_o A}{d_o} - \frac{D}{B_A} \right) - (k_a + k_b) D \\ \frac{V}{\alpha L} \frac{\partial E}{\partial t} &= \frac{1}{R_B} \left(\frac{b_o B}{e_o} - \frac{E}{B_B} \right) + k \frac{d_o D}{b_o B} - 2k_c e_o E^2 + 2k_d \frac{f_o}{e_o} F \\ \frac{V}{\alpha L} \frac{\partial F}{\partial t} &= \frac{1}{R_C} \left(\frac{c_o C}{f_o} - \frac{F}{B_E} \right) + k_a \frac{d_o}{f_o} D + k_c \frac{e_o^2}{f_o} E^2 - k_d D \end{aligned} \quad (6)$$

The initial conditions are:

$$\begin{aligned}
 A(y,0) &= g_1(y) & D(y,0) &= g_4(y) \\
 B(y,0) &= g_2(y) & E(y,0) &= g_5(y) \\
 C(y,0) &= g_3(y) & F(y,0) &= g_6(y)
 \end{aligned} \tag{7}$$

where the g_i may be zero, constant, or an impressed concentration gradient through the reactor length. In addition, equation (5) requires two boundary conditions. These are:

$$\begin{aligned}
 A(0,t) &= h_1(t) & \left(\frac{\partial A}{\partial y}\right)_{y=1} &= 0 \\
 B(0,t) &= h_2(t) & \left(\frac{\partial B}{\partial y}\right)_{y=1} &= 0 \\
 C(0,t) &= h_3(t) & \left(\frac{\partial C}{\partial y}\right)_{y=1} &= 0
 \end{aligned} \tag{8}$$

where the h_i are known functions of time.

This set of nonlinear coupled partial differential equations must be solved to obtain the desired concentrations as functions of dimensionless time and position. Because of the nonlinearities and the coupling that occurs through the reaction terms, the authors have been unable to obtain an analytical solution. It is not possible to use the Laplace Transform technique described previously (2) because of the nonlinearities resulting from the reaction terms. For these reasons, a finite difference method was used.

A detailed derivation of equations (5) and (6) as well as the initial and boundary conditions may be formed in reference (5).

D. Finite Difference Equations

The finite difference method used to solve equations (5) and (6) is the classical Crank Nicholson method (6). The resulting finite difference equations are of such length and complexity that they will not be presented here, however, a detailed derivation along with the resulting equation set may be found in reference (5). Computation was done on an IBM 360/50 system using Fortran IV, G level.

Briefly, the method of solution involved solving for all species at each point in the reactor for a given time step, j , then using these values to calculate concentrations of each species in the $j+1$ time step. In this manner numerical integration proceeded from one time step to the next.

Computation time for this method was found to be quite long due to the limited size of increments which had to be used to obtain convergence. It has been shown (6) that the following condition must be satisfied in order that the method converge:

$$\left(\frac{\Delta t}{\Delta y^2}\right) \leq \frac{1}{2}$$

Thus, for a Δy of 0.1 it is necessary to choose $\Delta t \leq 0.005$. This entails a large number of time steps and hence extremely large computation times. Because of this limitation, a less restrictive method of numerical integration such as that proposed by Liu (7) and Saul'yev (8) or by Peaceman and Rachford (9) may be used in future work. Such a program is now in development.

E. Calculation of the Moments

The first, second and third moments of each fluid phase species are calculated at various points in the vector bed by the computer program. The second and third moments are calculated about the first moment using the following expressions:

$$\mu_i(y) = \sum_t t c_i(y,t) / \sum_t c_i(y,t) \quad (9)$$

$$\sigma_i^2(y) = \sum_t t^2 c_i(y,t) / \sum_t c_i(y,t) - \mu_i^2(y) \quad (10)$$

$$\begin{aligned} \pi_i^3(y) = \sum_t t^3 c_i(y,t) / \sum_t c_i(y,t) - 3\mu_i(y)\sigma_i^2(y) \\ + 2\mu_i^3(y) \end{aligned} \quad (11)$$

The moments are to be used later in conjunction with experimental data to help predict the various parameters in the fluid dispersion model used.

III. COMPUTER RESULTS

A. Concentration Curves

The computer program generated values of concentration in the fluid and adsorbed phase for each species at various increments through the length of the reactor. Only the fluid phase concentrations were calculated because the difficulty in trying to measure adsorbed concentrations physically would make the computer values virtually impossible to check experimentally. Due to the extremely large number of

time steps necessary for convergence, computer output was not taken for every time step, but rather for every tenth of a residence time.

Two different conditions were examined. The first of these was the condition where oxygen is totally chemisorbed. That is, oxygen is desorbed from the surface of the carbon only in the form of CO or CO₂. Typical concentration curves for these runs are shown in Figure 1.

The second condition investigated was one in which oxygen was not all chemisorbed, that is, oxygen could desorb from the carbon surface without undergoing reaction. Typical results are given in Figures 2 and 3. Table 1 lists the parameters used to develop these figures.

Additional calculations were made, assuming both partial and total chemisorption to test the sensitivity of the program to changes in the input parameters. These results will be discussed later.

B. Moment Curves

The first, second and third moment for each active species in the fluid phase was calculated at each incremental point in the reactor bed. Although concentration values were printed only at every tenth of a residence time, concentrations at each time step were used to calculate the moment by means of equations (9), (10), and (11).

TABLE 1

Summary of Parameters
Used to Develop Figures 2 and 3

Pe_A	=	156.2	α	=	0.46
Pe_B	=	142.8	B_A	=	0.223
Pe_C	=	113.6	B_B	=	0.285
L	=	1.0 ft.	B_C	=	0.248
k_a	=	0.45 sec^{-1}	k_1	=	$0.22 \text{ ft}^6/\text{mole}^2\text{sec}$
k_b	=	0.15 sec^{-1}	k_d	=	0.11 sec^{-1}
k_c	=	$0.13 \text{ ft}^3/\text{mol}\cdot\text{sec}.$			
a_o	=	$1.0 \text{ mols}/\text{ft}^3$			
b_o	=	$1.0 \text{ mols}/\text{ft}^3$			
c_o	=	$1.0 \text{ mols}/\text{ft}^3$			
v	=	$0.05 \text{ ft}/\text{sec}$			
d_o	=	$1.0 \text{ mols}/\text{ft}^2$			
e_o	=	$1.0 \text{ mols}/\text{ft}^2$			
f_o	=	$1.0 \text{ mols}/\text{ft}^2$			
R_A	=	1.28 sec			
R_B	=	1.12 sec			
R_C	=	1.76 sec			

Figure 4 shows the moment curves which were calculated from Figure 1 corresponding to the case where oxygen is totally chemisorbed. Figure 5 is a similar graph corresponding to the case in which oxygen is partially chemisorbed. This figure has been calculated from the results shown in Figure 2.

IV. RESULTS

The results presented in this paper are not to be considered as absolute values because many of the parameters used in the solution of the finite difference program are not known and can only be obtained experimentally. Rather, the purpose of the results presented is to indicate the relative effect of the various parameters on the individual concentrations. Thus the purpose is to indicate which parameters are the most significant ones and their relative effect on the system.

The results shown in Figures 1 - 3 are in agreement with some preliminary experimental findings and they do not exhibit any unexpected characteristics.

The sensitivity of the system to various parameters which could be varied physically was studied and the results are presented below. The effect of the velocity is shown in Figures 6, 7, and 8. The effect of the pulse duration is shown in Figure 9. In addition, the effect of various void

fractions was studied, but for the range of void fractions which are believed to be realized physically, the effect on the system was not significant. For example, for a variation in void fraction from between 0.30 to 0.60, the relative change in any concentration was less than ten to fifteen percent. This last statement was made for the condition of total chemisorption of O_2 .

Figure 10 shows the case of no reaction either in the gas stream or on the solid surface. Equal pulses of each active species were used. This situation is equivalent to that treated by Chao (10).

Figure 11 presents the moments which were generated from the concentration curves shown in Figure 10.

V. DISCUSSION

For the case where oxygen is totally chemisorbed, the first moments of each species were found to be linear within a few percent deviation. For those cases in which oxygen is partially chemisorbed, the deviation from linearity becomes greater. The greatest deviation from linearity of the first moment was found to be about 20%. Linearity of the first moment has been predicted by Chao (10) and by Levenspiel and Smith (11). However, Chao assumes no reaction and a δ input to obtain his linear expression for the first moments while Levenspiel and Smith assume a δ input and/or infinite

reactor. Thus any deviation from linearity in the results presented here might be attributed to the fact that the input used was not a δ function and a reactor of finite length was studied.

The sensitivity of the moments is of great importance if the impulse-response technique is to be used in an experimental program. A significant change in at least one of the moments was noted for each parameter varied with the exception of the void function. Varying a parameter did not change each of the moments proportionally as shown in Figures 6, 7, and 8.

No attempt was made to study the effect of temperature, although it is felt that this will eventually be one of the most important parameters in the experimental program, because of its effect on so many of the parameters used in this model. The effect of temperature is one of the principle objectives of an experimental program that is currently under investigation.

In conclusion, a finite difference program has been developed which in its general form permits the simulation of complex flow-reaction systems. Furthermore, as a preliminary to an experimental program, a carbon-oxidation reaction has been simulated and the relative effect of various flow and reaction parameters on the system has been investigated.

ACKNOWLEDGMENT

The authors wish to acknowledge Dr. Harold E. Hoelscher, Dean of the School of Engineering of the University of Pittsburgh, whose previous work provided the basis for this study and who first suggested this research topic. The financial assistance provided by the National Science Foundation through Grant Number GK-2140 and the National Aeronautics and Space Administration through Grant Number NGL-39-011-002 is appreciated. Finally, the support of the Computer Center of the University of Pittsburgh is gratefully acknowledged.

NOTATION

A	a/a_0 , dimensionless concentration of O_2 in fluid phase or gaseous reactant concentration per unit volume of bed
a	concentration of O_2 in fluid phase per unit volume of bed
B	b/b_0 , dimensionless concentration of CO in fluid phase or slope of the adsorption isotherm
b	concentration of CO in fluid phase per unit volume of bed
C	c/c_0 , dimensionless concentration of CO_2 in fluid phase or concentration of gaseous species C per unit volume of bed
C*	equilibrium concentration of species C per unit volume of bed
c	concentration of CO_2 in fluid phase per unit volume of bed
D	d/d_0 , dimensionless concentration of O_2 in the adsorbed phase or diffusion coefficient, ft^2/sec
d	concentration of O_2 in adsorbed phase per unit surface area
E	e/e_0 , dimensionless concentration of CO in the adsorbed phase
e	concentration of CO in the adsorbed phase per unit surface area
F	f/f_0 , dimensionless concentration of CO_2 in the adsorbed phase
f	concentration of CO_2 in the adsorbed phase per unit surface area
g(y)	initial condition
h(t)	boundary conditions
k	reaction rate coefficients
L	overall reactor length, ft.

Pe	vL/D , Peclet number, dimensionless constant
R	resistance to mass transfer, sec
r	reaction rate in gas phase, concentration/unit time
r_s	reaction rate on solid surface, concentration/unit time
S	source or sink term, concentration/unit time
t	$v\theta/L$, dimensionless time
v	interstitial fluid velocity, ft/sec
W	adsorbed species concentration per unit surface area
x	variable of position in the reactor, ft
y	x/L , dimensionless variable of position in the reactor

Greek Letters

α	void fraction of the bed
δ	dirac function
θ	time, sec
$\mu(y)$	first moment, sec
$\sigma^2(y)$	second moment, sec ²
$\pi^3(y)$	third moment, sec ³

Subscripts

i	species i
o	reference concentration
a, b, c, d	refer to reactions in adsorbed phase
l	fluid phase reaction

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Figure 1

Dimensionless concentration vs. dimensionless
length for total chemisorption of O_2

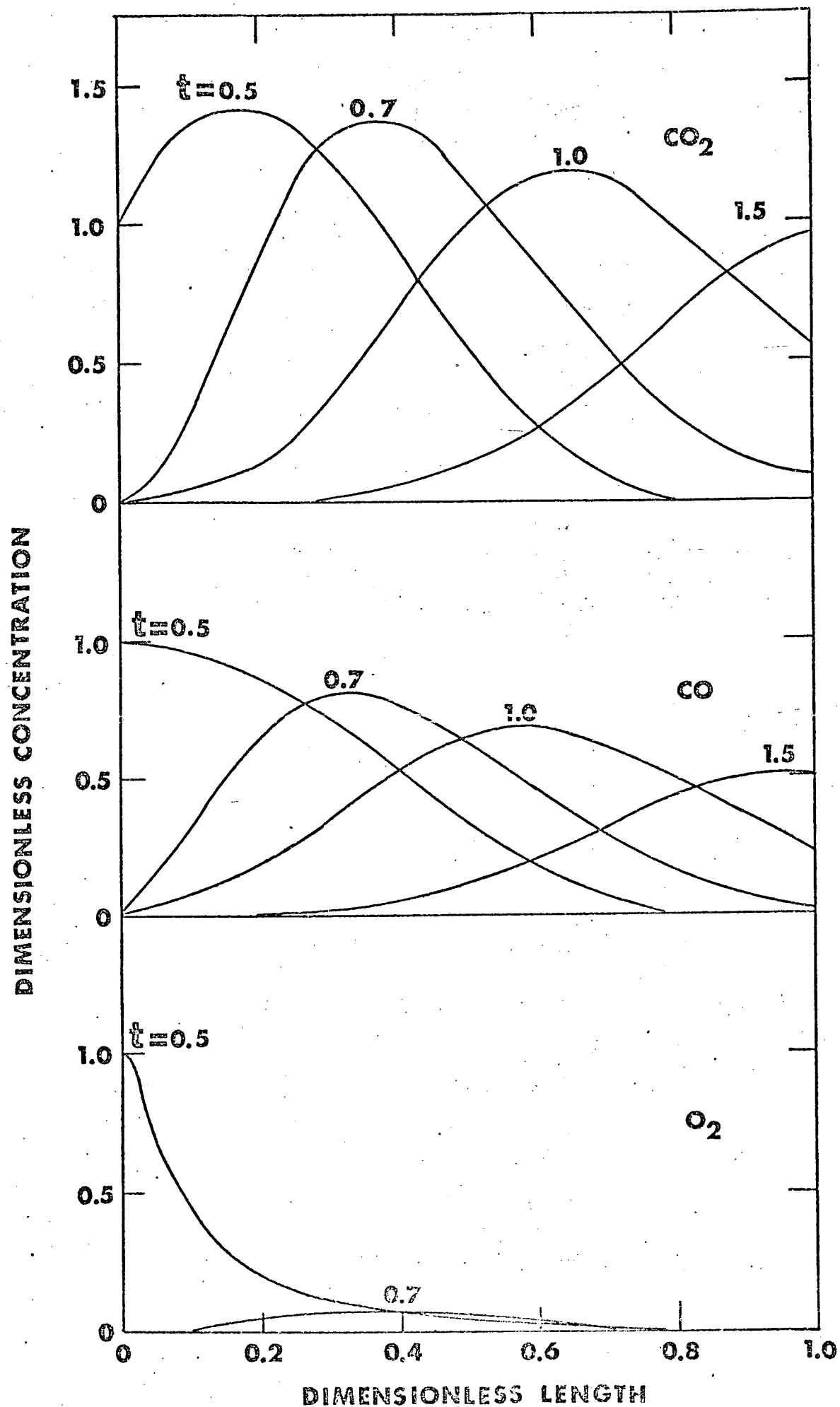


Figure 2

Dimensionless concentration vs. dimensionless
length for partial chemisorption of O_2

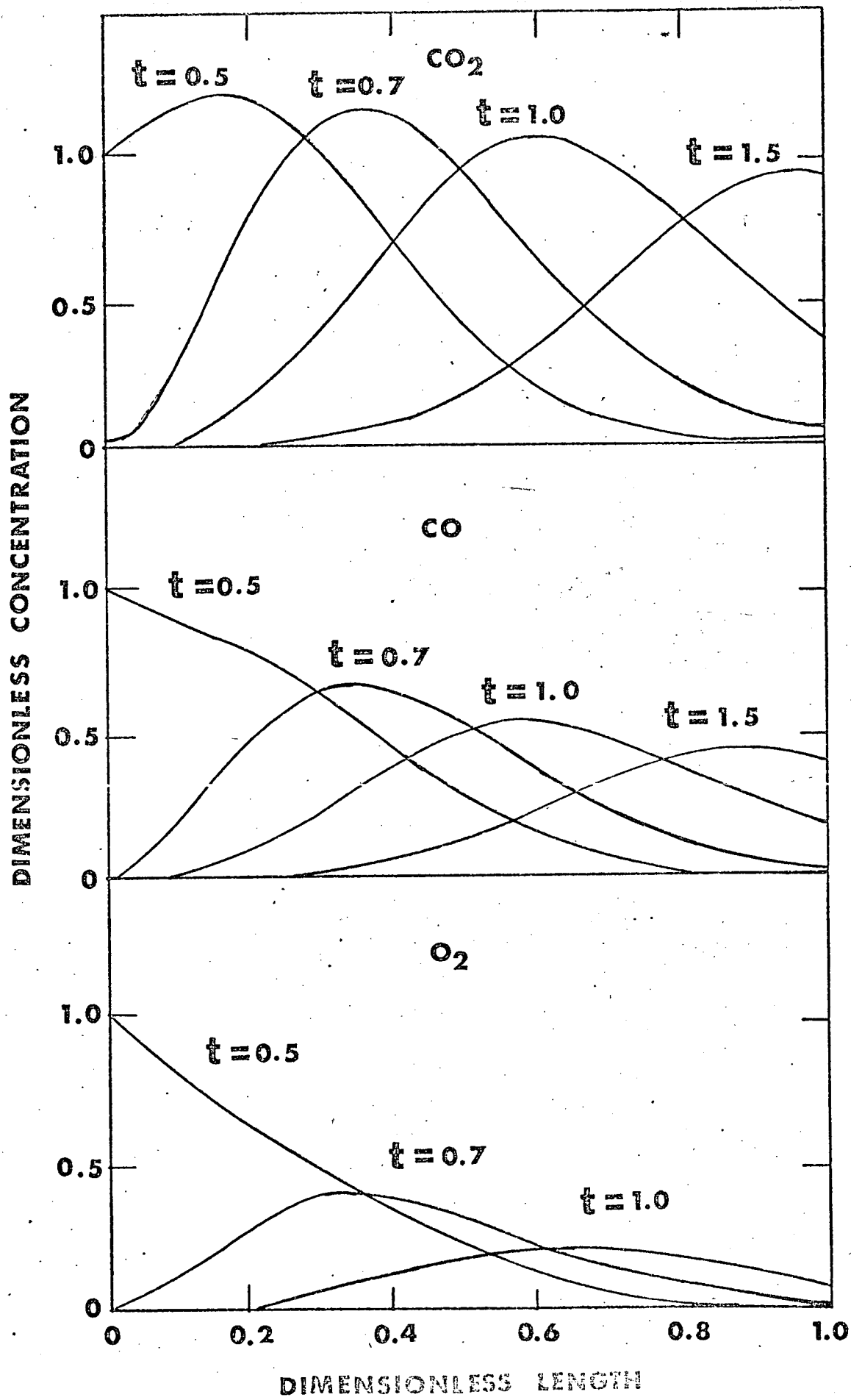


Figure 3

Dimensionless concentration vs. residence time
for the case of partial chemisorption of O_2

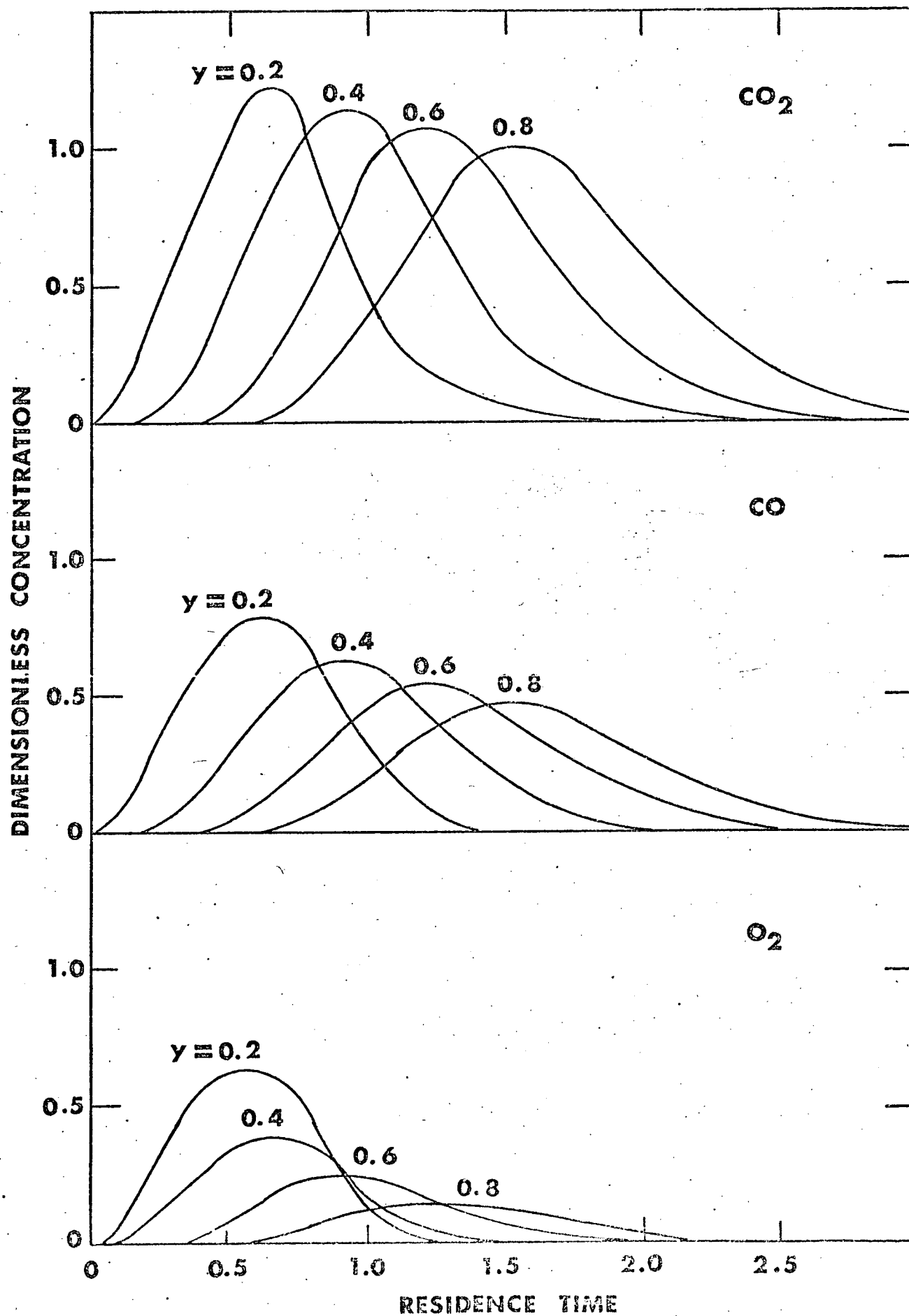
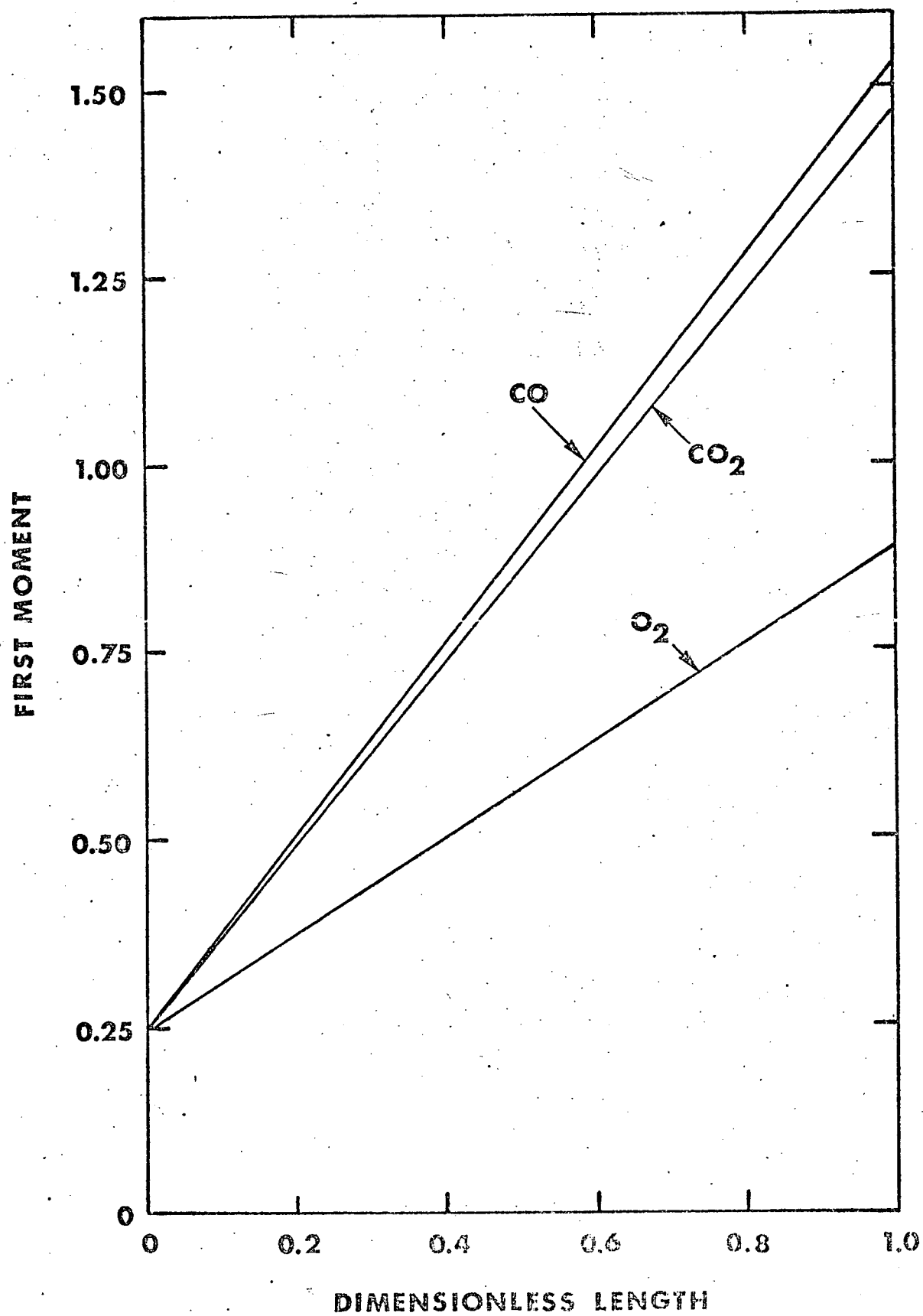
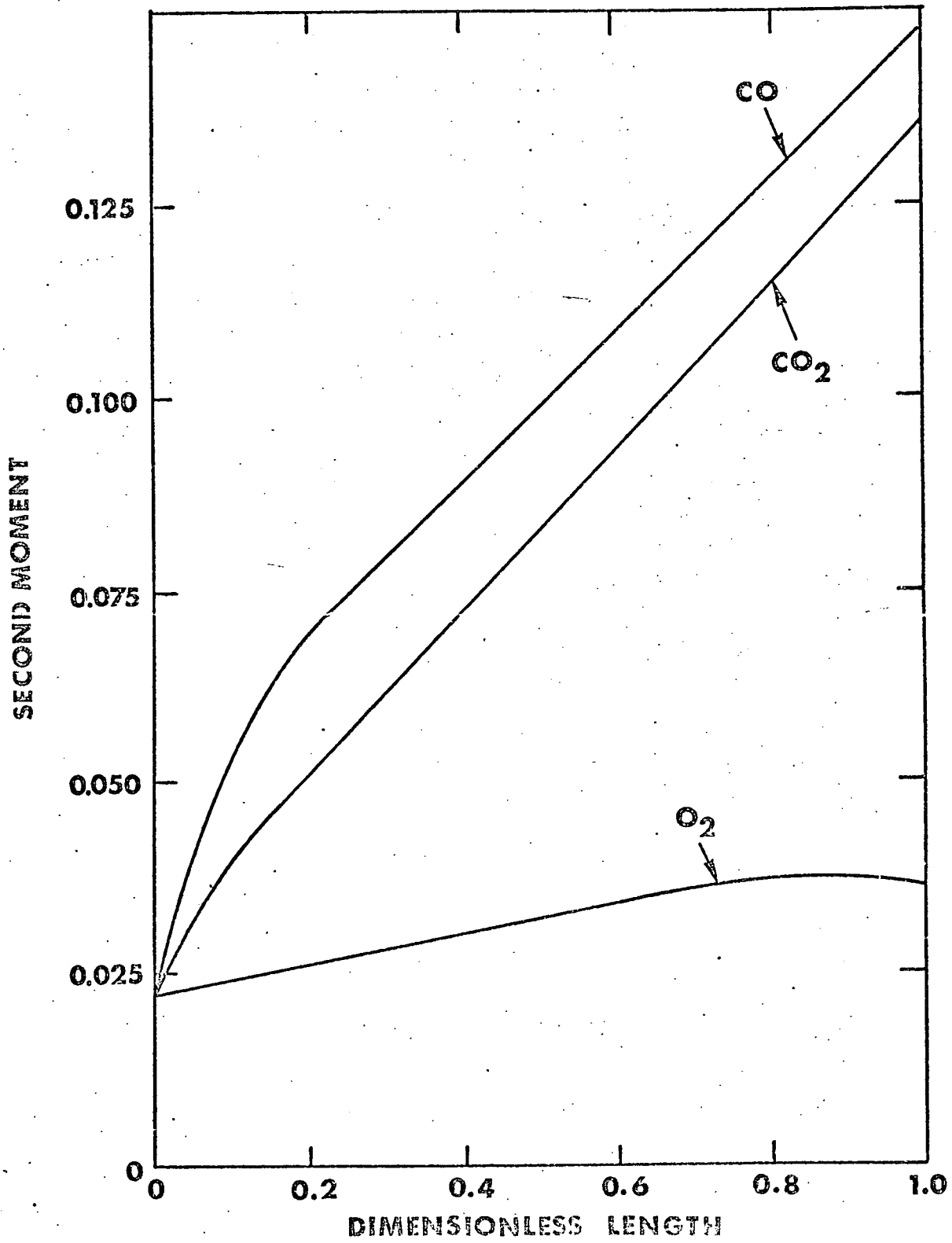


Figure 4

First, second, and third moments vs. dimensionless
length for total chemisorption of O_2





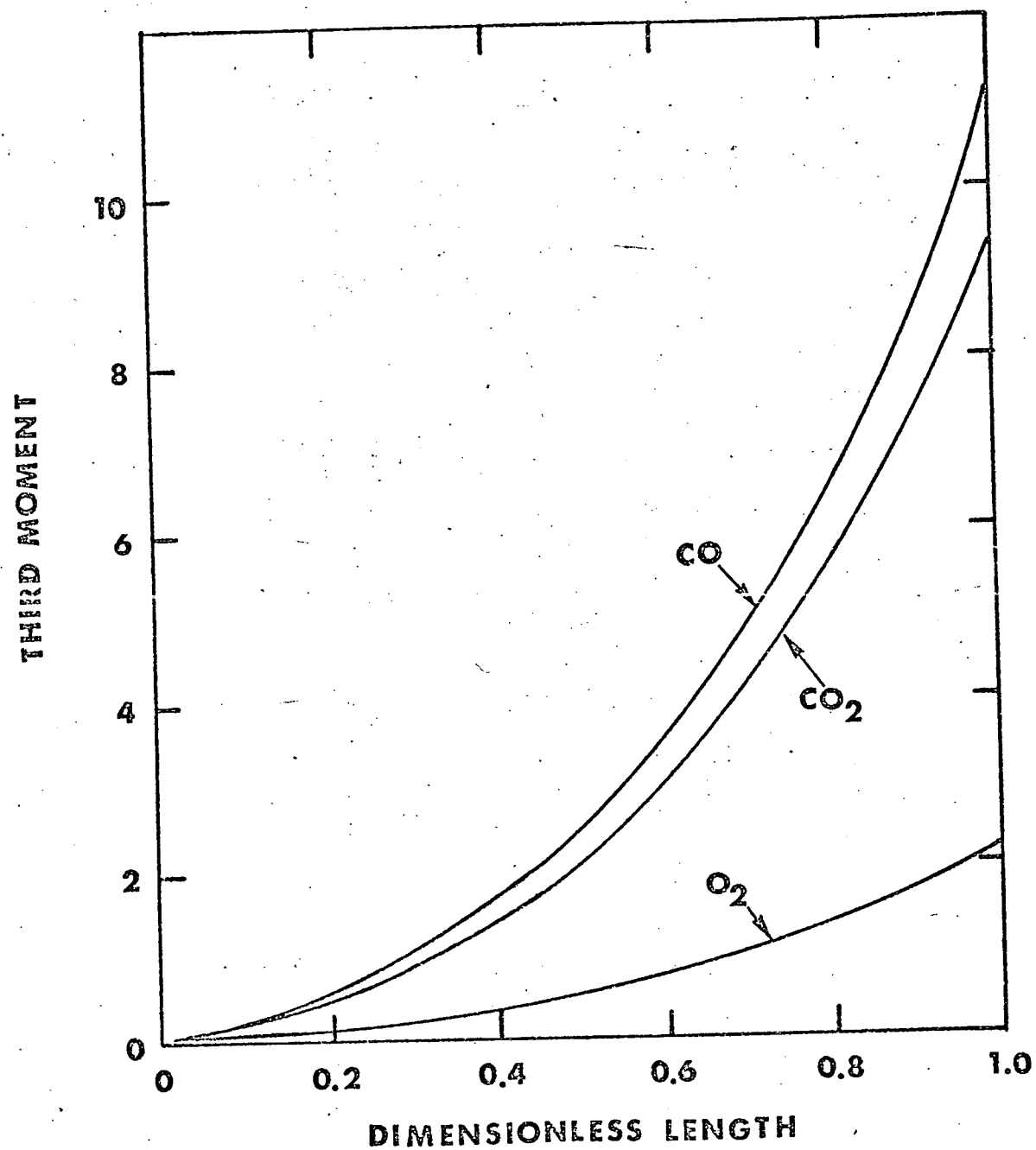
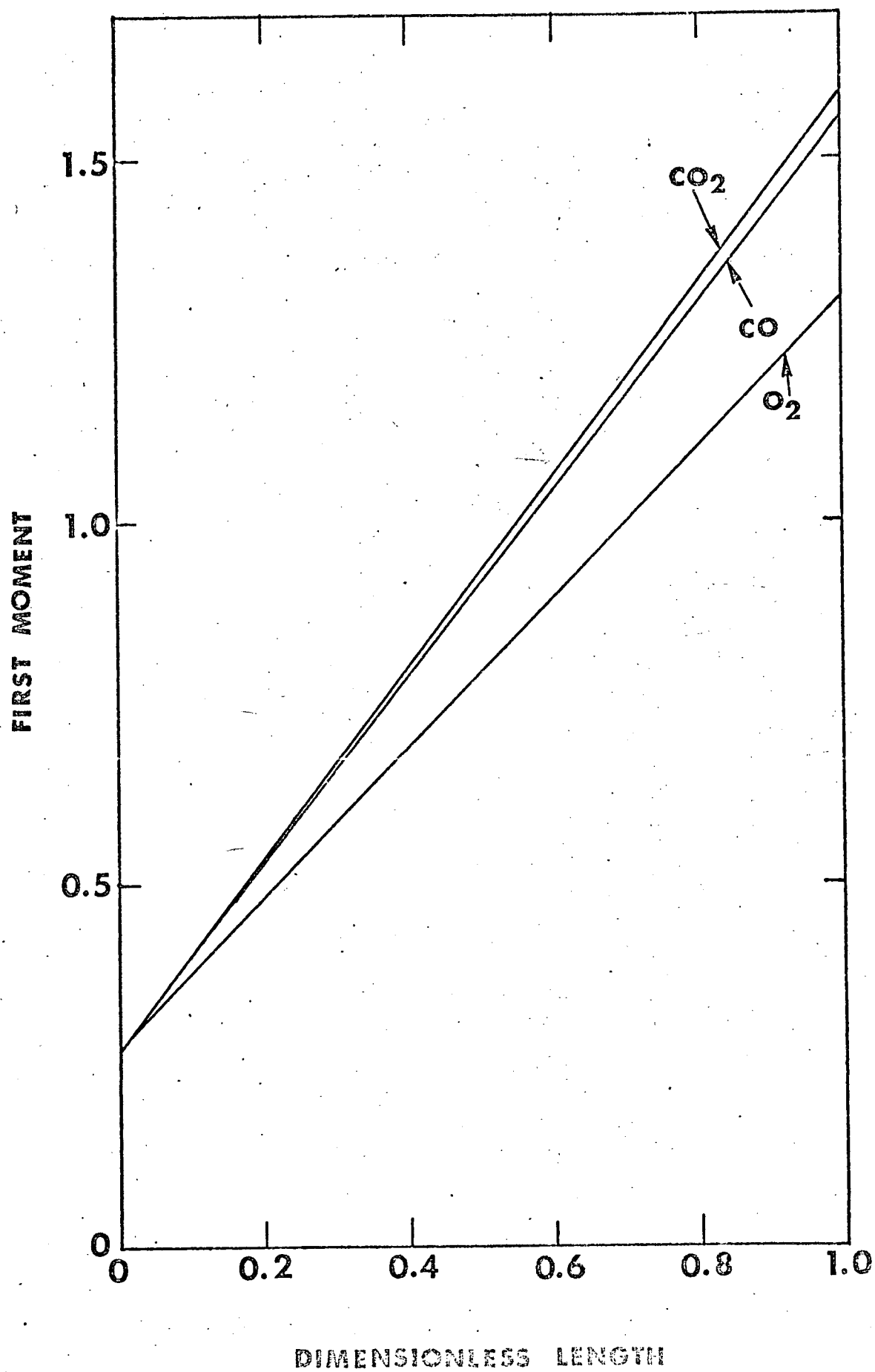
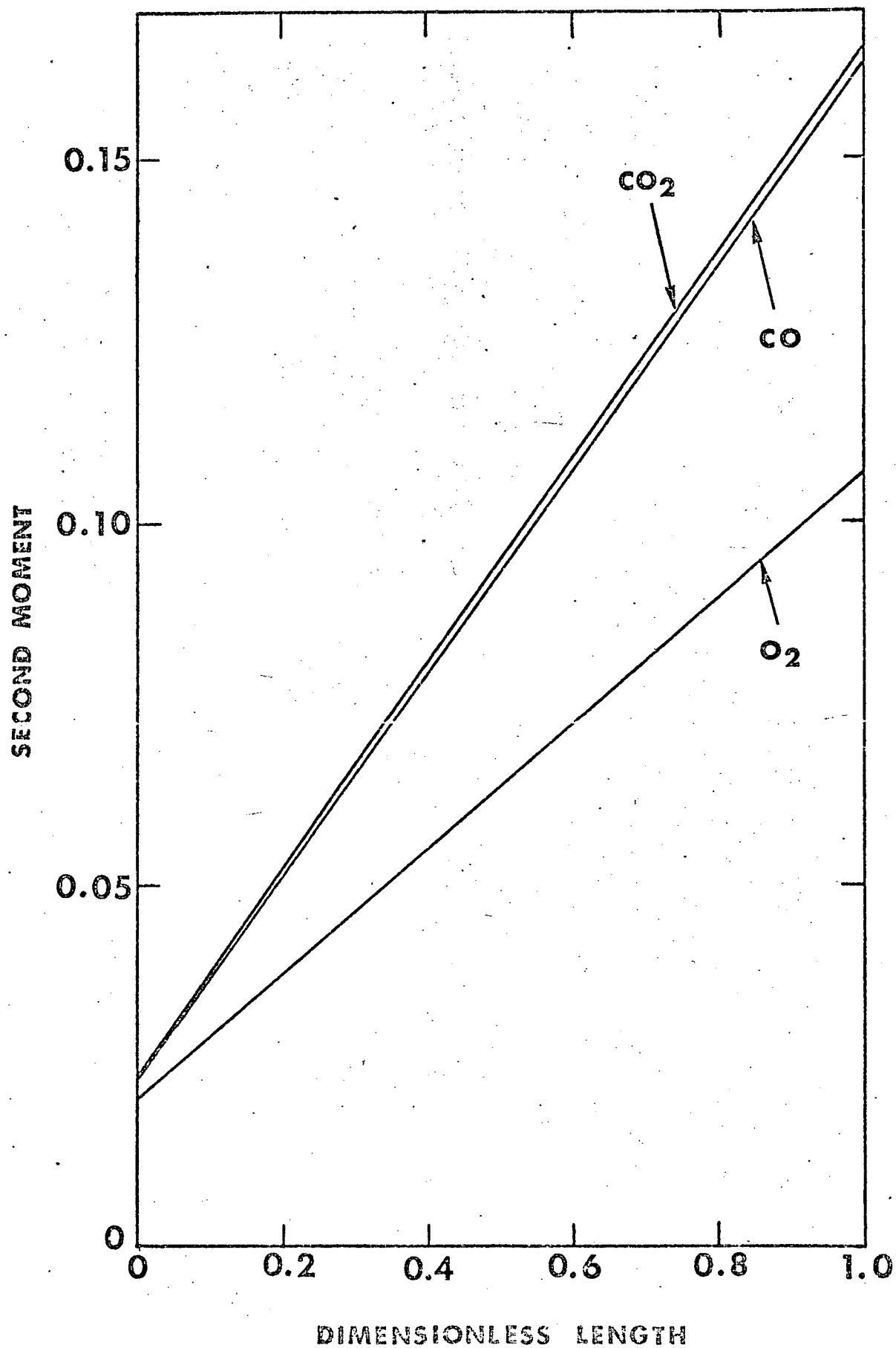


Figure 5

First, second, and third moments vs. dimensionless
length for partial chemisorption of O_2





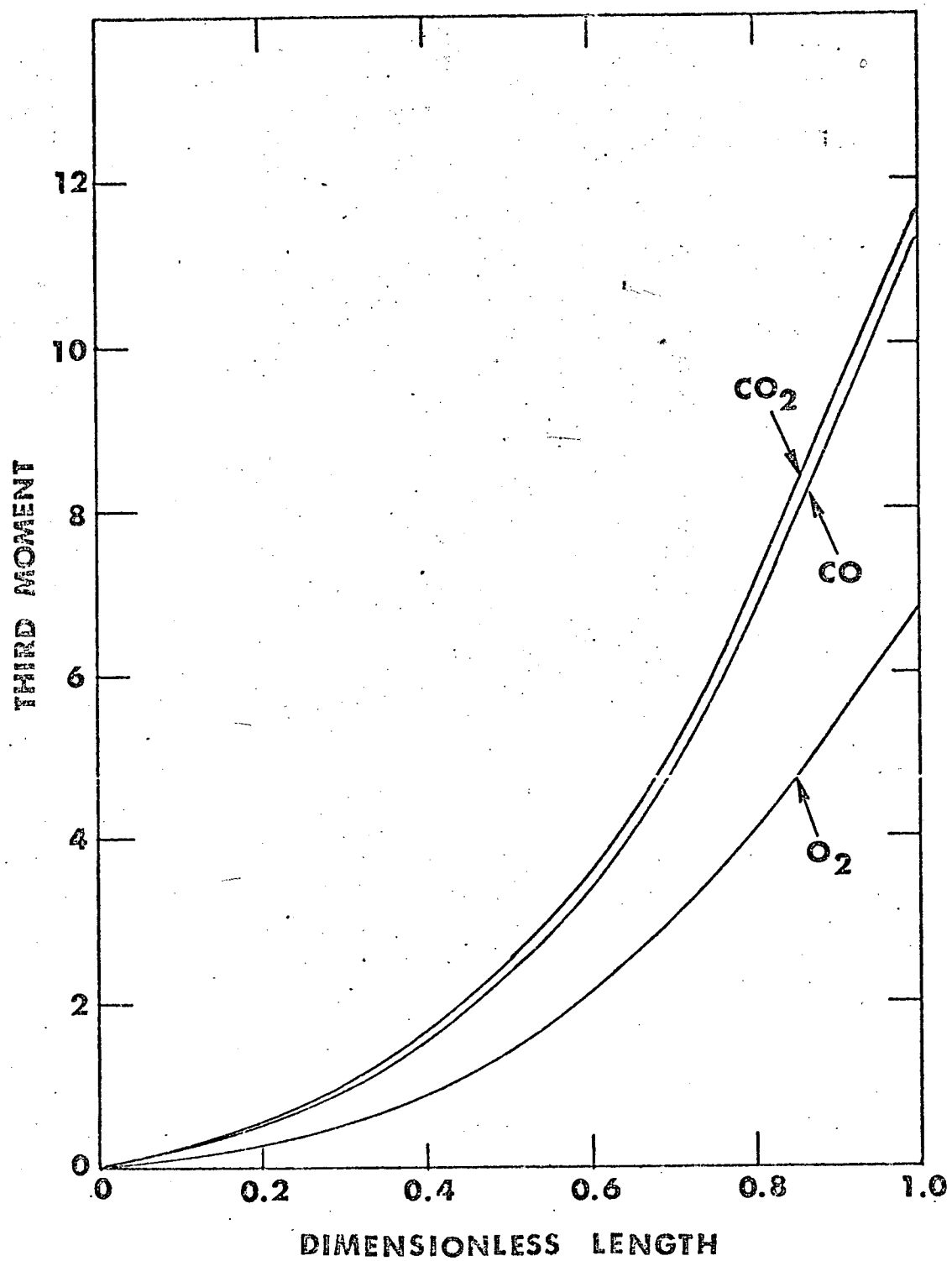
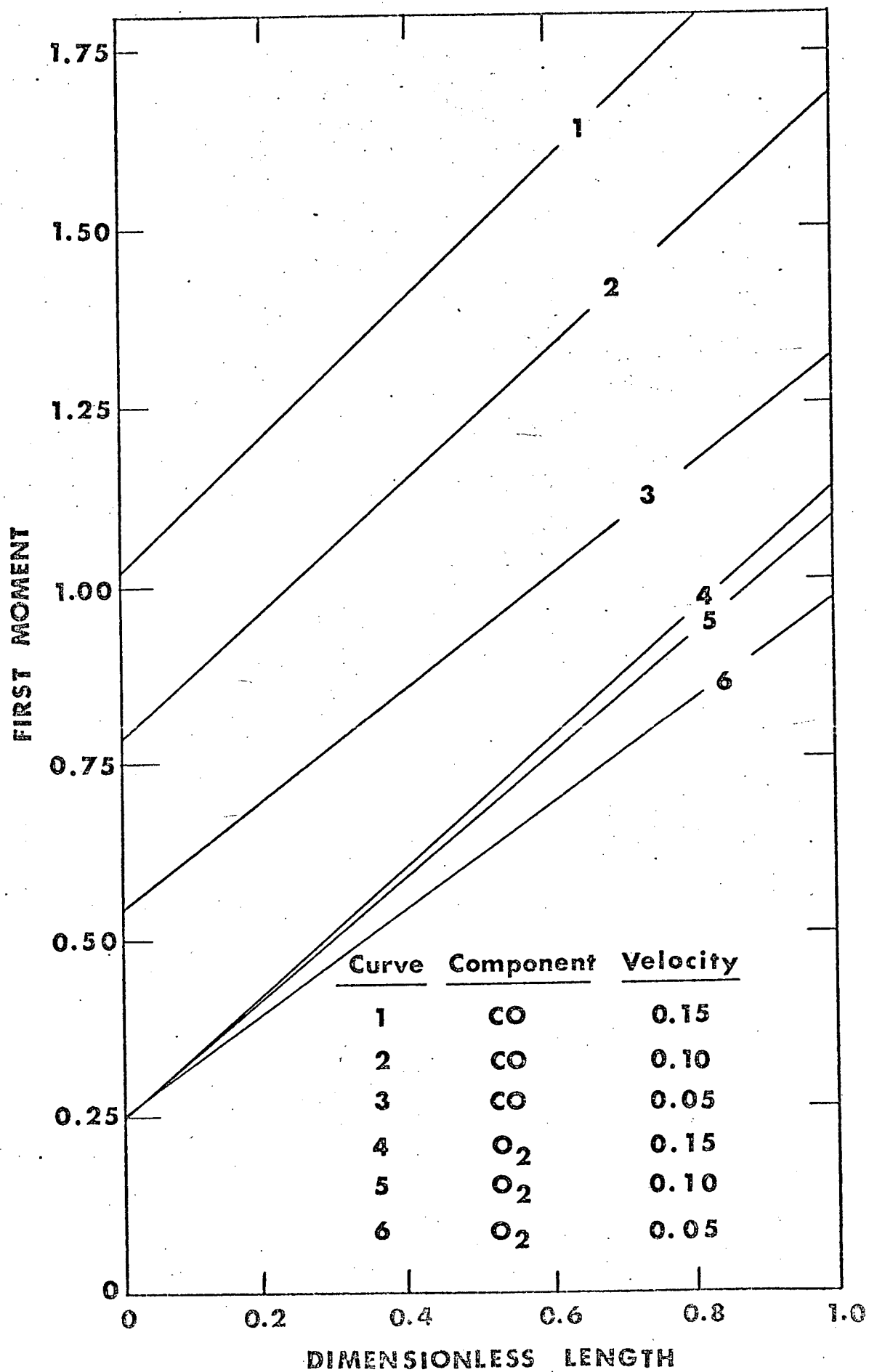


Figure 6

First moments vs. dimensionless length
for various flow velocities



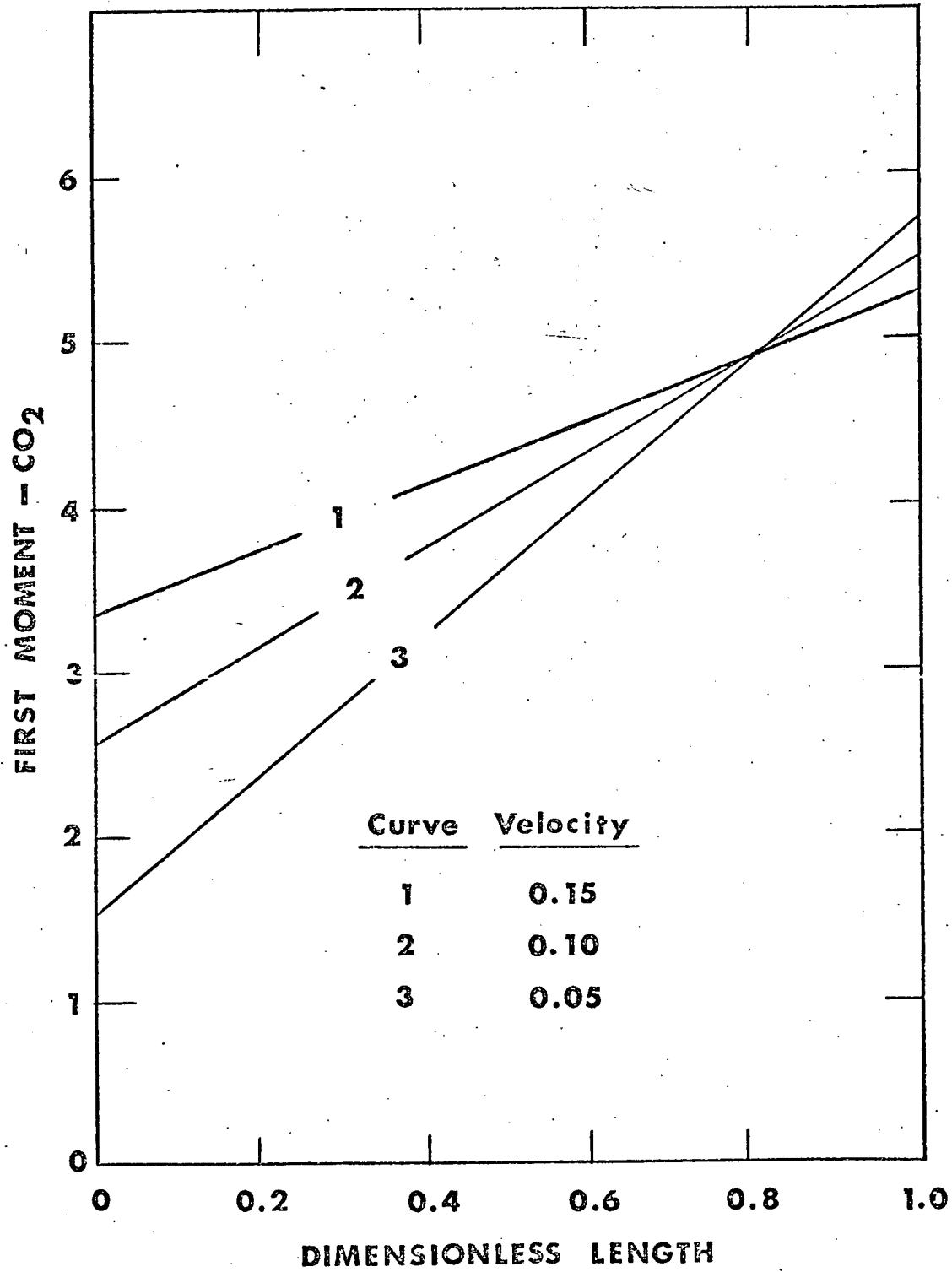
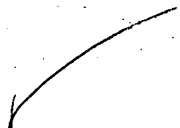
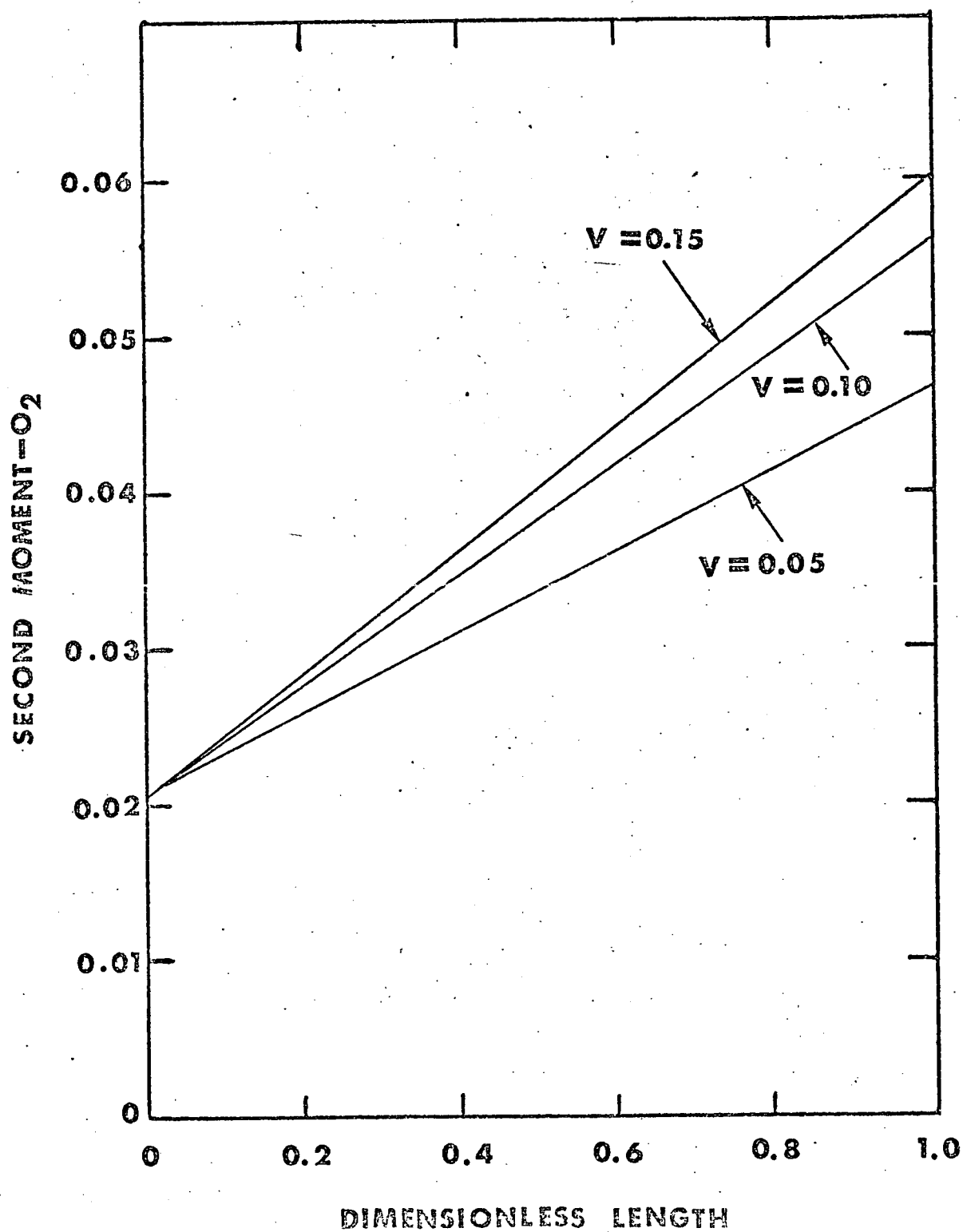
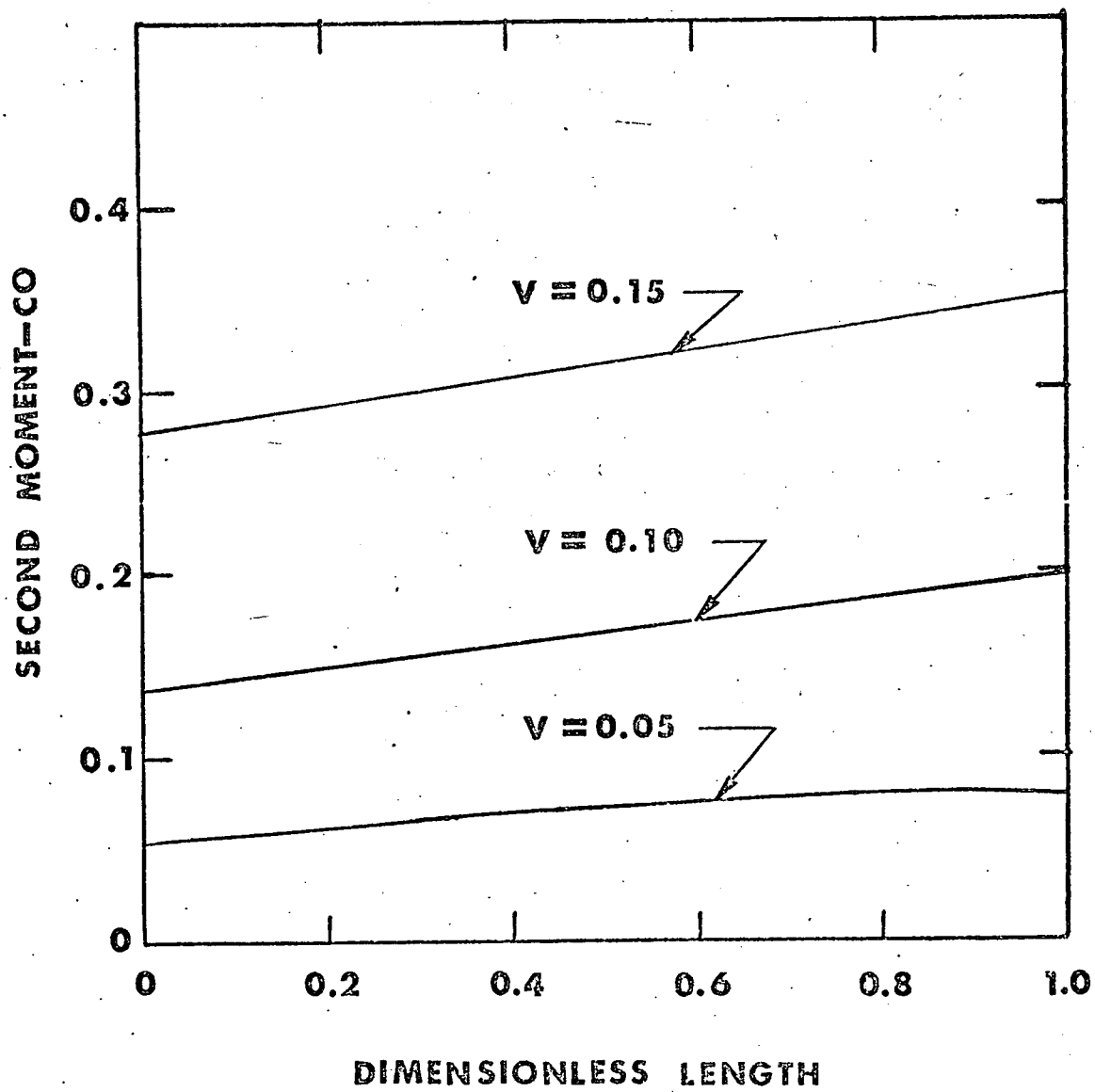


Figure 7

Second moments vs. dimensionless
length for various flow velocities







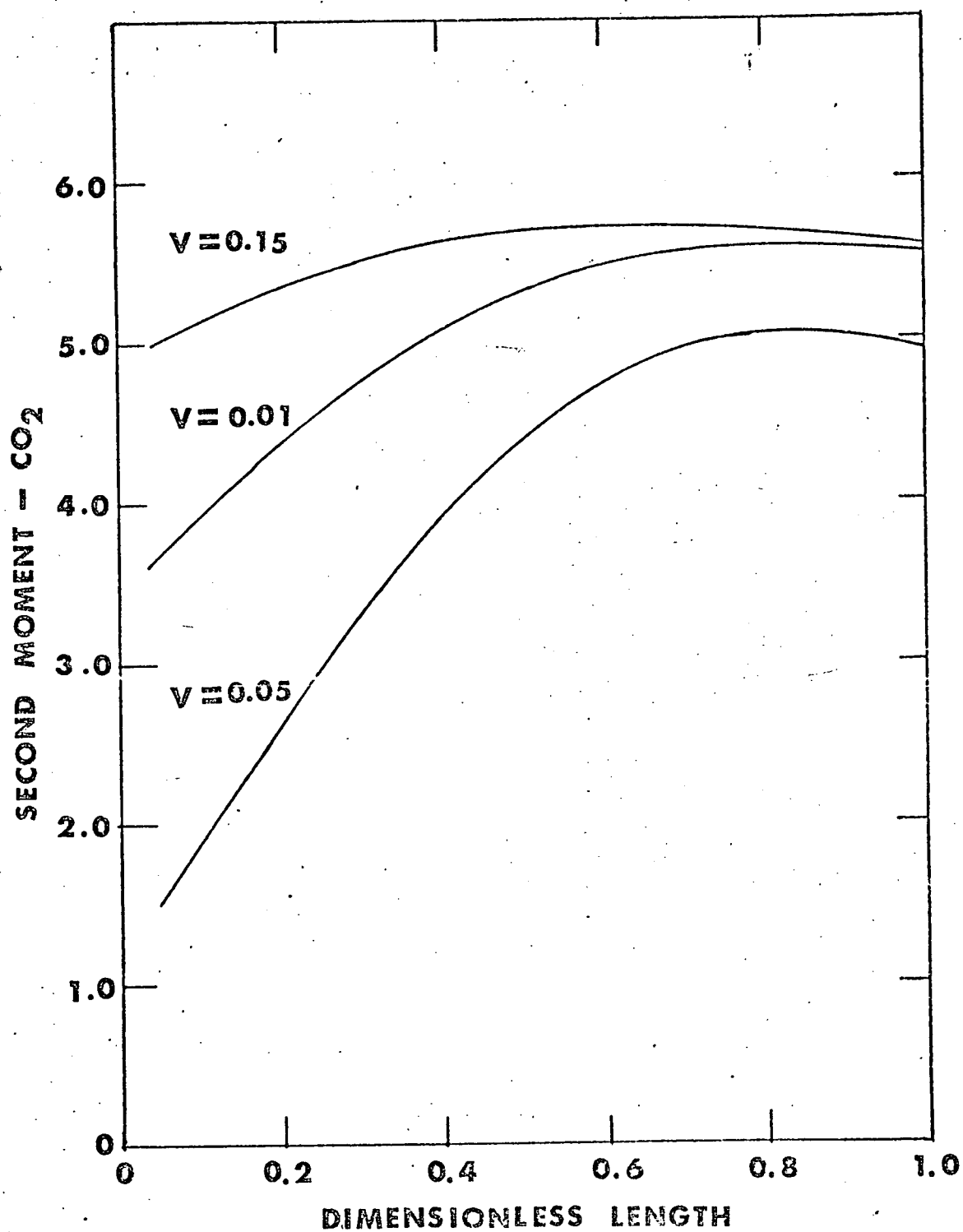
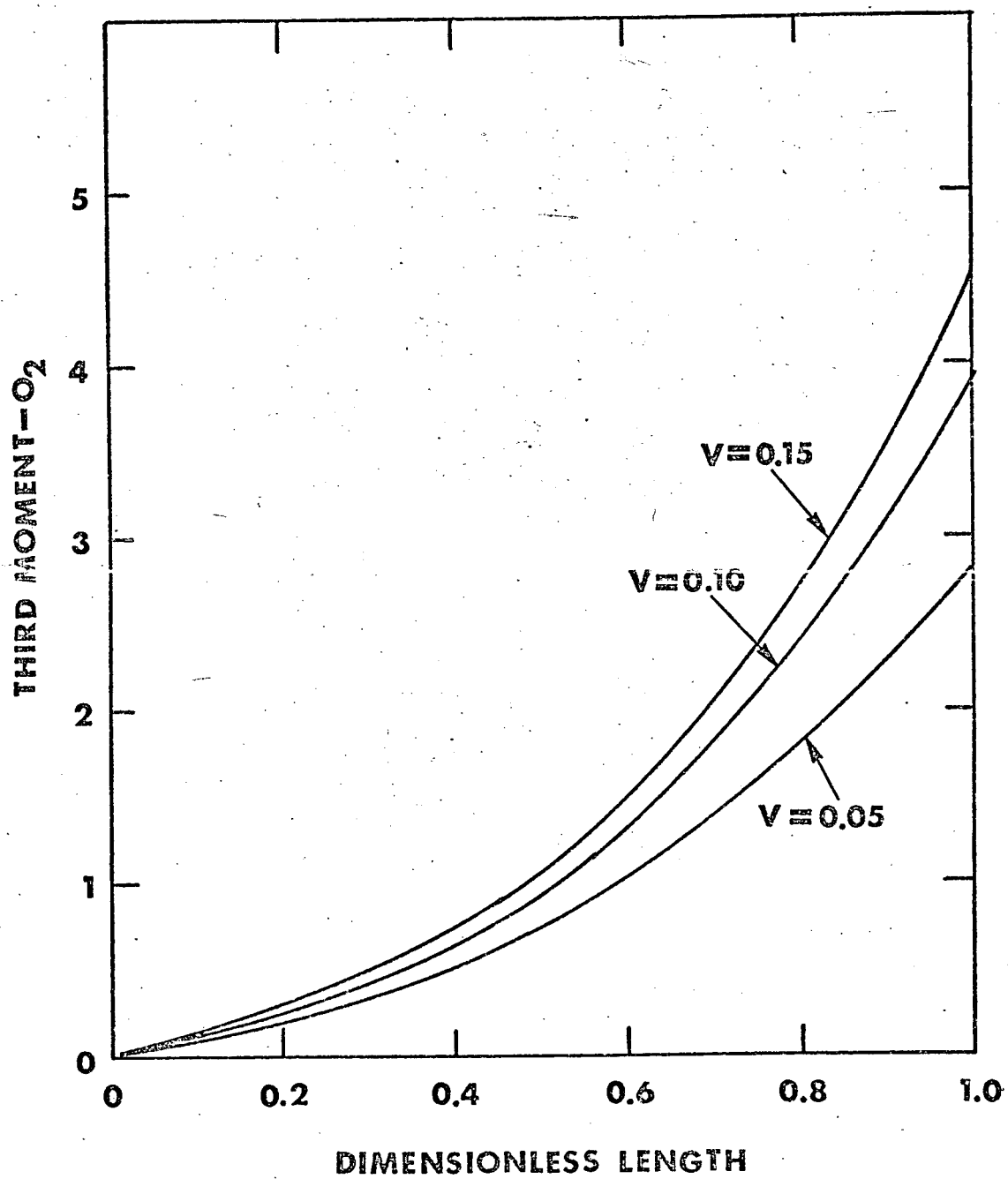
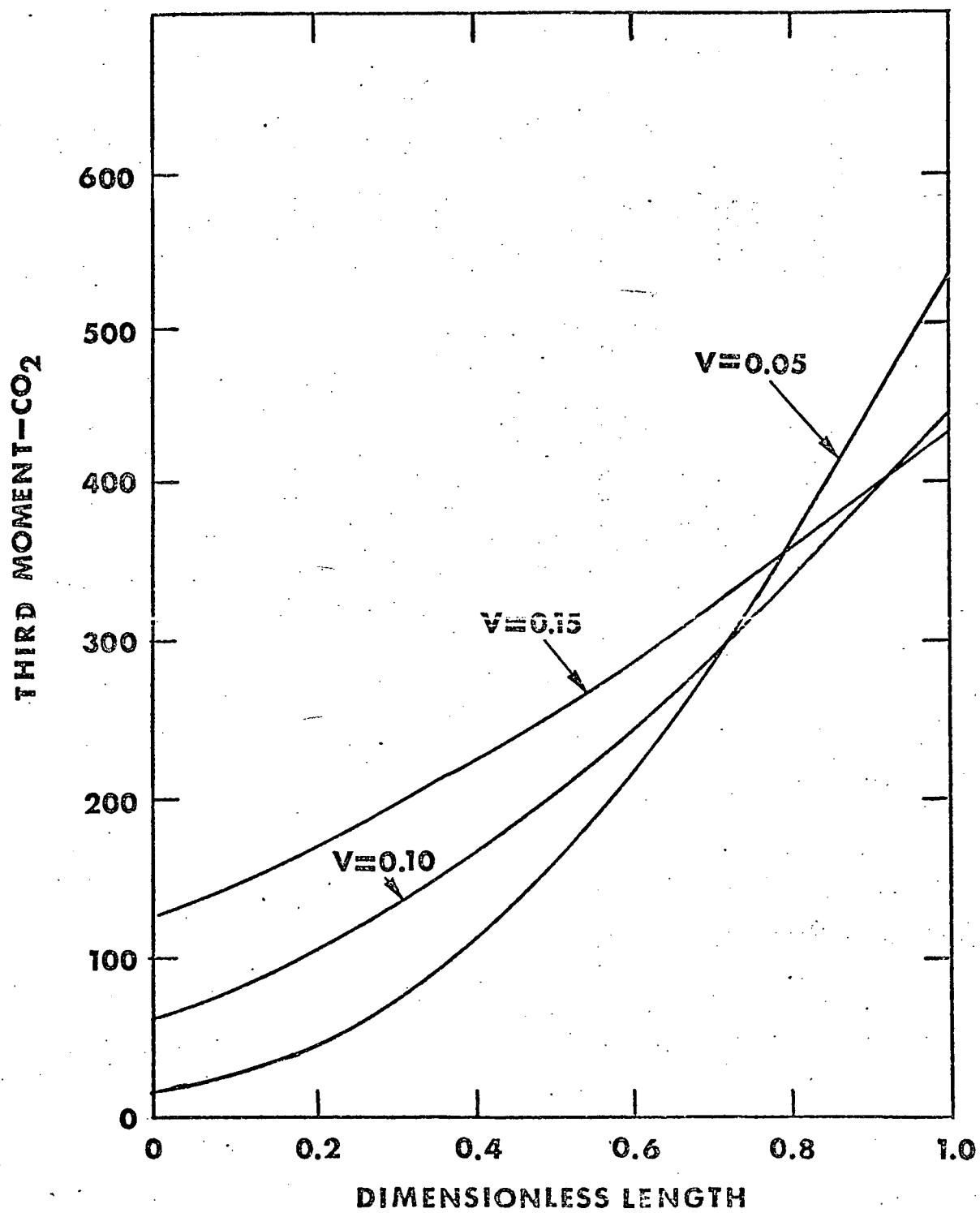


Figure 8

Third moments vs. dimensionless
length for various flow velocities





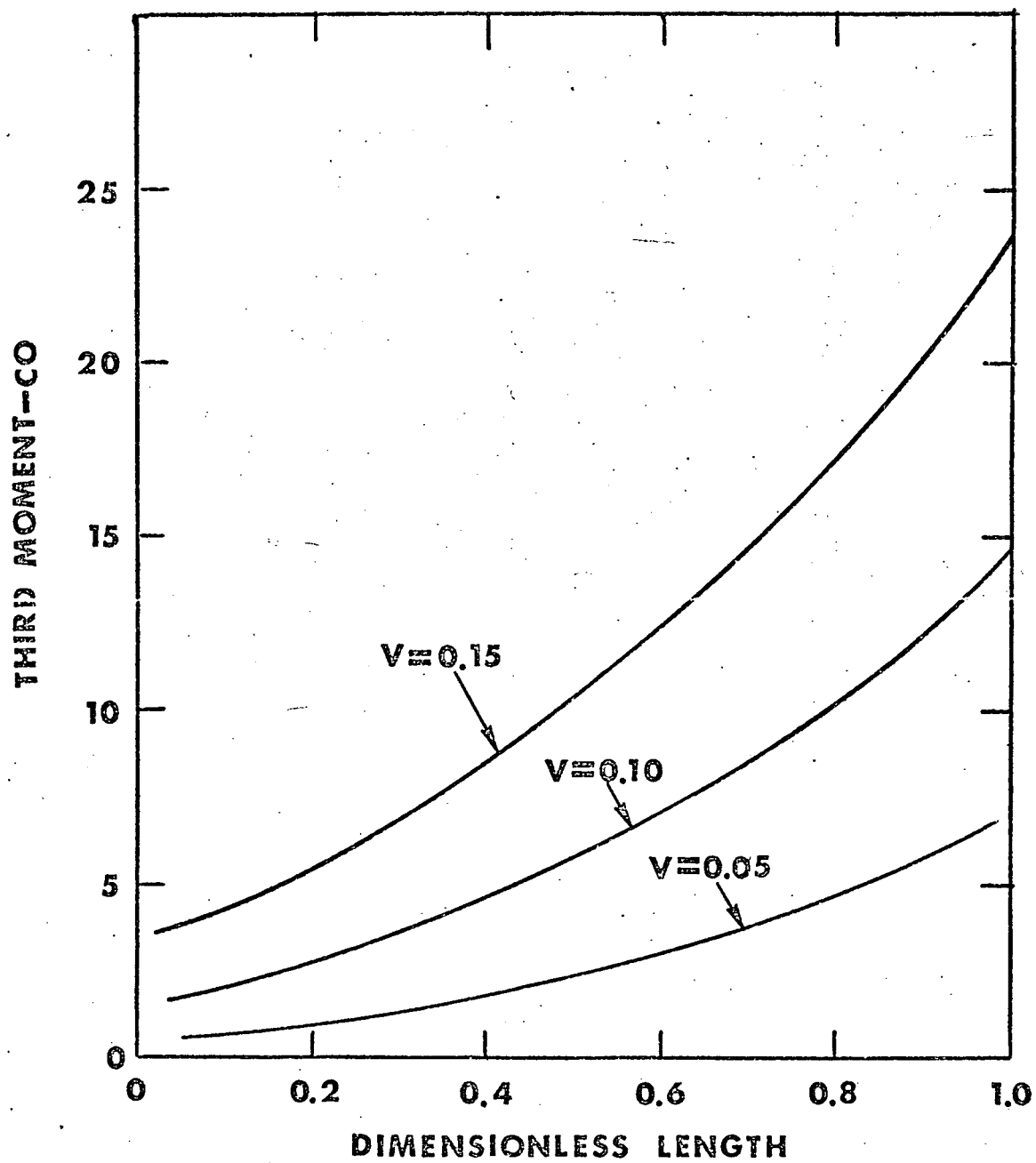
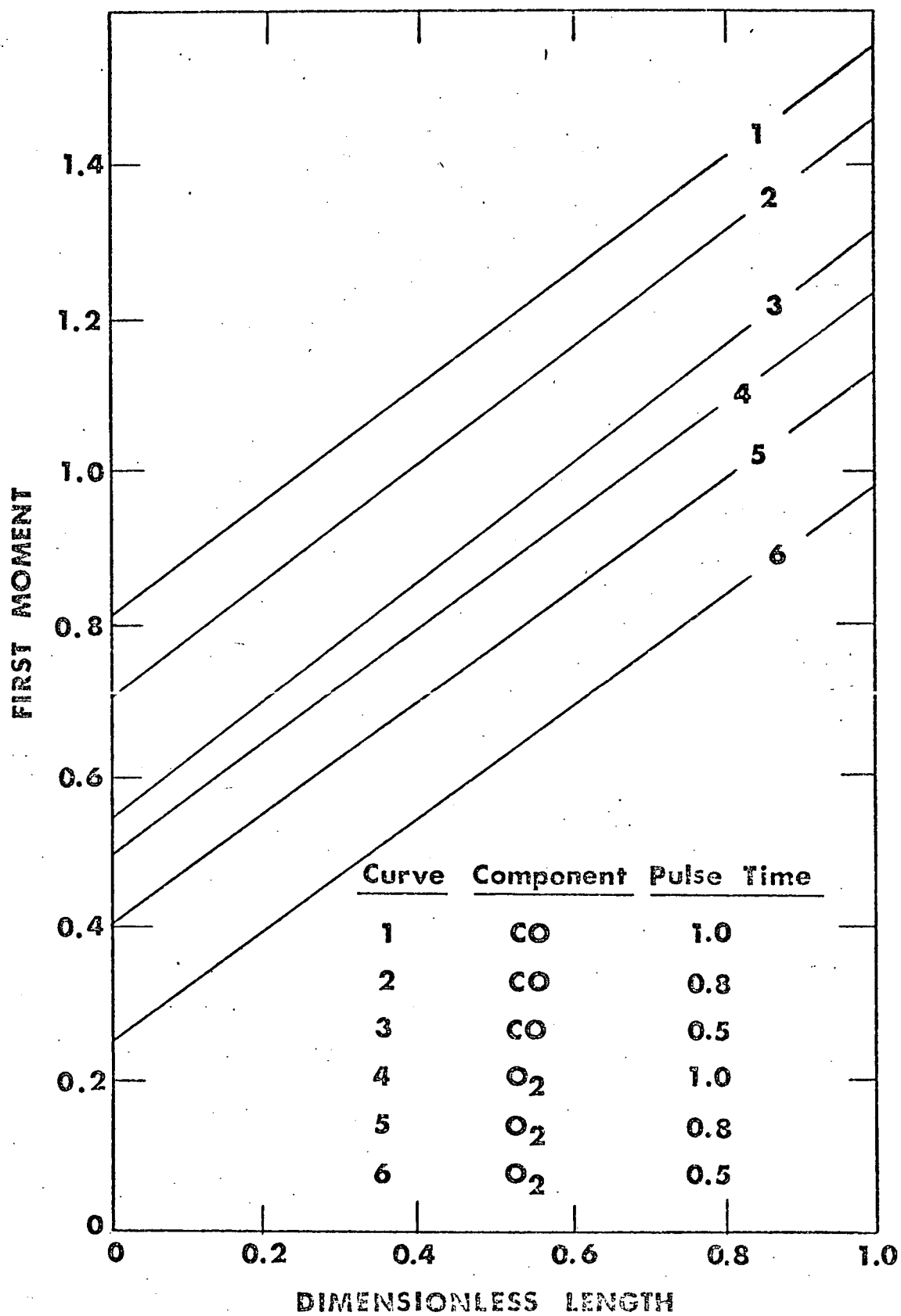


Figure 9

First moment vs. dimensionless
length for various pulse durations



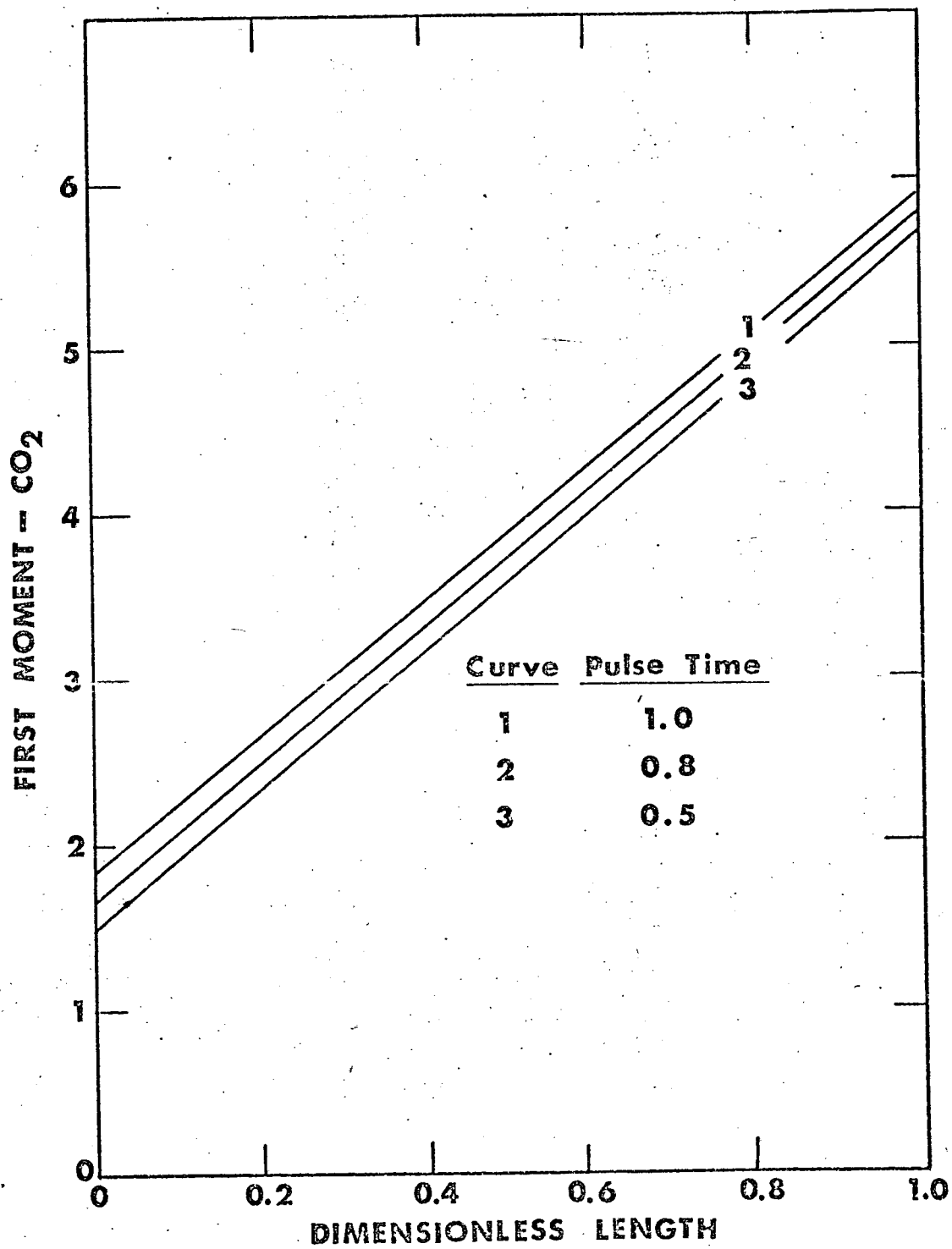


Figure 10

Dimensionless concentration vs. residence time
for the case of no chemical reaction

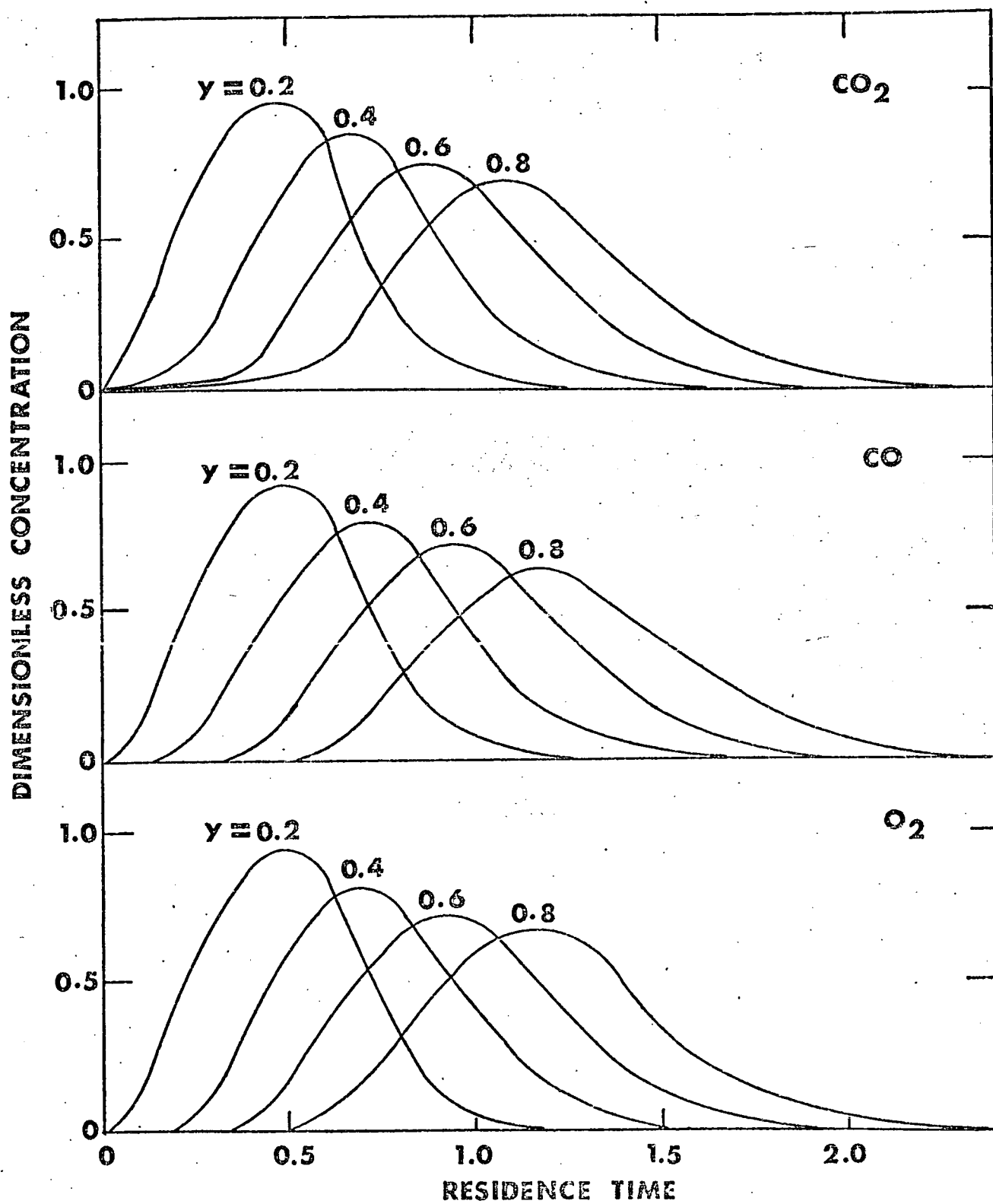


Figure 11

First, second, and third moments vs. dimensionless
length for the case of no chemical reaction

